



Study on the structure and property of lead tellurium alloy as the positive grid of lead-acid batteries

W.X. Guo^a, D. Shu^{a,*}, H.Y. Chen^a, A.J. Li^a, H. Wang^b, G.M. Xiao^b,
C.L. Dou^b, S.G. Peng^b, W.W. Wei^b, W. Zhang^b, H.W. Zhou^b, S. Chen^b

^a School of Chemistry and Environment, Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, South China Normal University, Guangzhou, Guangdong 510006, China

^b Zhuzhou Smelter Group Co., Ltd., Zhuzhou Hunan 412004, China

ARTICLE INFO

Article history:

Received 28 May 2008

Accepted 4 August 2008

Available online 24 September 2008

Keywords:

Lead alloy

Grid alloy

Smelting

Lead-acid batteries

ABSTRACT

A series of novel Pb–Te binary alloys with different contents of tellurium (0.01–1.0 wt.%) were investigated as the positive grid of a lead acid battery. The microstructure of Pb–Te alloys was observed using a polarizing microscope. The morphology of the corrosion layers and corroded surfaces of Pb and Pb–Te alloy electrodes were analyzed by scanning electron microscopy (SEM) following the corrosion test. The electrochemical properties of Pb–Te alloys and Pb–Te–Sn alloy in sulfuric acid solution were investigated by cyclic voltammetry (CV), open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), alternating current voltammetry (ACV), and linear sweeping voltammetry (LSV). The results indicate that the introduction of tellurium results in grain refinement, increased corrosion resistance, and an accelerated oxygen evolution reaction for the Pb–Te binary alloys. The passive films formed on Pb–Te–Sn alloy shows improved performances in comparison to those on Pb–Ca–Sn alloy.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, the major grid material for lead acid batteries is the lead–calcium–tin (Pb–Ca–Sn) alloy. This alloy is especially suitable for the maintenance-free lead-acid battery, because it leads to lower water consumption from the electrolyte. However, an undesirable characteristic is that the Pb–Ca–Sn alloy may suffer deterioration due to severe corrosion at high temperatures [1]. Furthermore, it is easy to form a high impedance passive film composed of Pb(II) oxide between the positive grid and the active materials under deep charge–discharge conditions. As a result, new additives have been sought for introduction to the grid alloys to improve their performance. Rare earths such as Sm and Ce, regarded as effective additives, can inhibit the corrosion of the alloy and decrease the resistance of the anodic Pb(II) oxide film [2,3]. The addition of Ag to a Pb–Ca–Sn alloy can enhance its corrosion resistance, and increase the creep resistance, thereby improving battery durability at high temperatures [4]. It is reported that the addition of tellurium to lead can improve its durability, mechanical strength, and anti-corrosive ability. As an appropriate component for the lead grid alloy, tellurium has been reported by Bashtavelova and Winsel [5], but no further detailed report has been published regarding its

modified mechanism under operation condition. The structure and property of Pb–Te binary alloys with various contents of tellurium (0.01–1.0 wt.%) were investigated in detail in this paper. In addition, the characteristics of the passive film formed on the surface of a Pb–Te–Sn alloy in sulfuric solution were investigated.

2. Experimental

2.1. Preparation of the testing alloys

Pb–Te binary alloys with different contents of tellurium were processed by melting the mixtures of pure lead (99.99 wt.%) and pure tellurium (99.99 wt.%) in an electrical furnace under an argon gas atmosphere at 800 K for 15 min, cooling down to room temperature, and served as working electrodes. Pb–Te alloy as the master alloy was mixed with Sn (99.9 wt.%) to form the homogeneous Pb–Te–Sn alloy. Another testing alloy was the traditional Pb–Ca–Sn alloy, which was manufactured by doping the Pb–Ca master alloy with Sn. The sample alloys were cast in a steel mould in two designs: one was a rod with diameter 8.0 mm and length 16 mm, which was used for the electrochemical experiments; the other was a rectangular plate with dimensions 20 mm × 20 mm × 2 mm for use in the corrosion test. The composition of each alloy is listed in Table 1.

2.2. Microstructure

The metallographic samples were prepared from the rod alloys, one end of which was mechanically polished by 1000# and 2000# SiC emery papers. These samples were then chemically polished using a 1:1 (by volume) acetic acid/hydrogen peroxide solution, and etched with a solution containing 9 g of ammonium molybdate, and 15 g of citric acid in 90 g of distilled water. The structure of the alloys was observed using a Nikon LV-UEPT polarizing microscope.

* Corresponding author. Tel.: +86 20 39310212; fax: +86 20 39310187.
E-mail address: dshu@scnu.edu.cn (D. Shu).

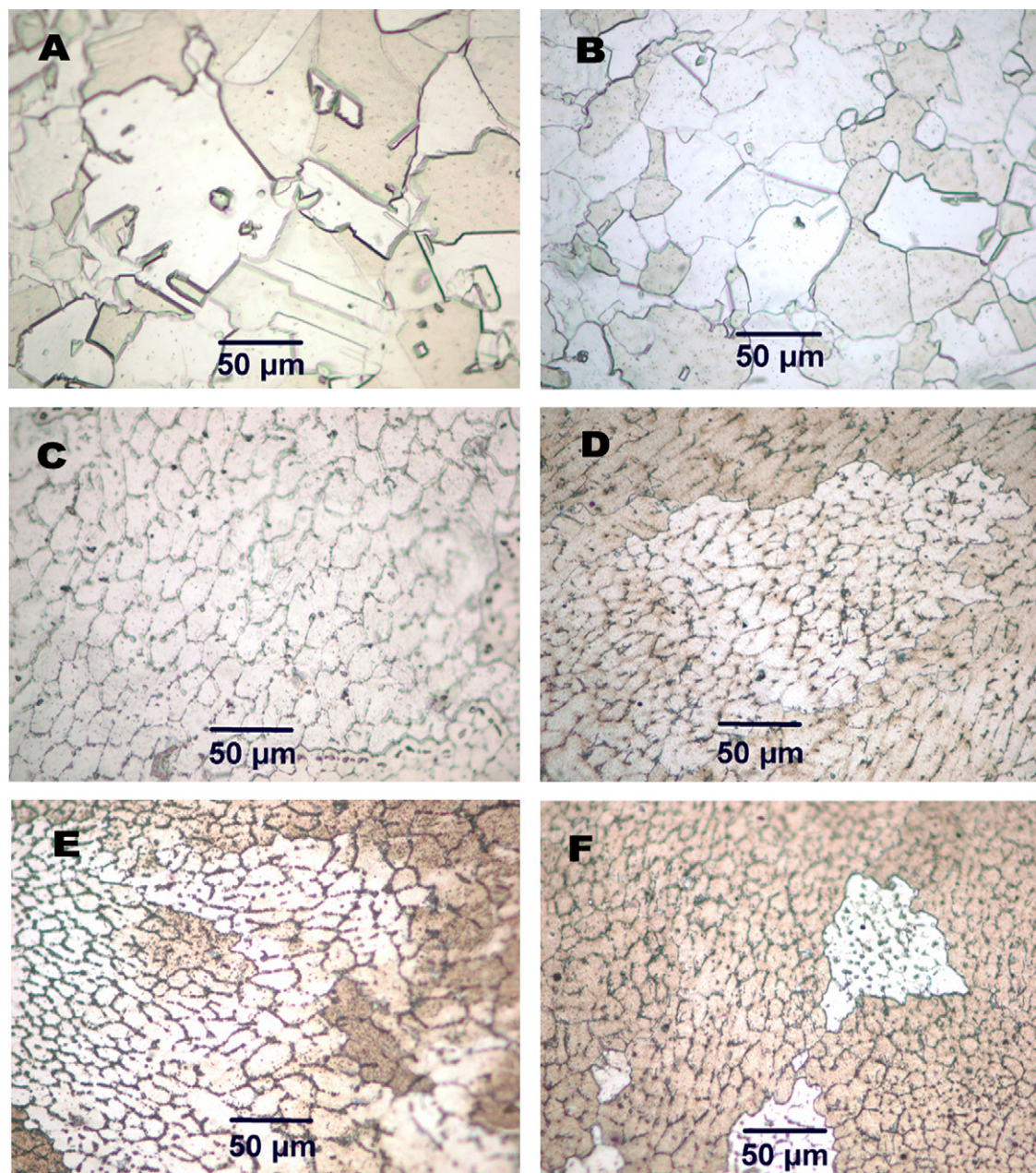


Fig. 1. Micrographs of Pb and Pb–Te alloys with different Te contents. (A) Pb; (B) Pb–0.01 wt.%Te; (C) Pb–0.03 wt.%Te; (D) Pb–0.1 wt.%Te; (E) Pb–0.3 wt.%Te; (F) Pb–1.0 wt.%Te.

2.3. Electrochemical experiments

A three-electrode configuration was used for the electrochemical experiments. The working electrode was a rod of lead alloy sealed in epoxy resin except for the

working surface, which was one end of the rod; the other end was welded with a copper wire to connect the instrument. The counter electrode was a platinum plate (0.5 cm²). The reference electrode was a Hg/Hg₂SO₄ electrode: all potentials reported in this paper were referred to this electrode. The electrolyte was 1.28 g cm^{−3} H₂SO₄ solution prepared from H₂SO₄ and double-distilled water. Before each test, the working electrodes were mechanically polished by 1000# and 2000# SiC emery papers, then washed with double-distilled water, and a cathodic potential of −1.2 V was applied for 10 min in order to eliminate the oxide formed during pretreatment. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), alternating current voltammetry (ACV), and linear sweeping voltammetry (LSV) measurement were performed using a PGSTAT30 (Autolab, Eco Chemie B.V. Company).

2.4. Corrosion test

Corrosion test was conducted in five cells in series connection. Each cell was assembled with two positive plate electrodes and two negative plate electrodes. The negative electrodes were pure lead plates, and the positive electrodes were Pb–Te plates. The corrosion test was carried out with a constant current of 10 mA cm^{−2} at a constant temperature of 60 °C for 20 days. The corrosion layer of one corroded elec-

Table 1
Composition of the testing alloys

Alloys	Contents of the additives (wt.%)		
	Te	Ca	Sn
1# Pb	–	–	–
2# Pb–Te	0.01	–	–
3# Pb–Te	0.03	–	–
4# Pb–Te	0.10	–	–
5# Pb–Te	0.30	–	–
6# Pb–Te	1.00	–	–
7# Pb–Te–Sn	0.03	–	0.90
8# Pb–Ca–Sn	–	0.08	0.90

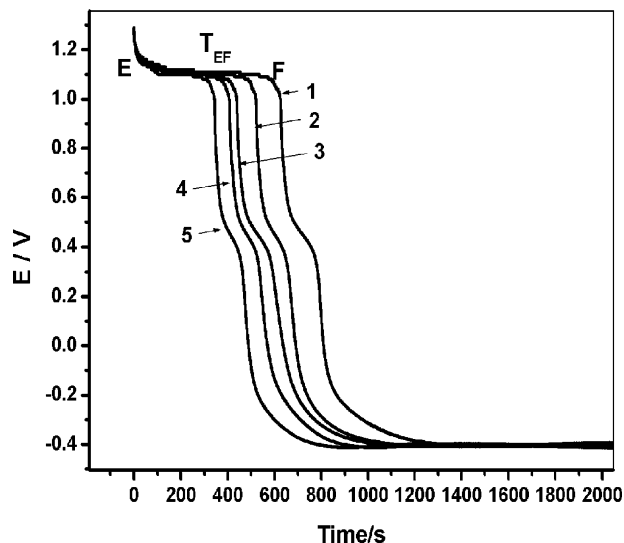


Fig. 2. The open circuit decay curves for the self-discharge of Pb and Pb–Te electrodes after 1 h charging at 1.3 V in 1.28 g cm^{-3} H_2SO_4 solution. 1, Pb; 2, Pb–0.01 wt.%Te; 3, Pb–0.03 wt.%Te; 4, Pb–0.3 wt.%Te; 5, Pb–1.0 wt.%Te.

trode for each alloy was removed using a boiling solution containing 4 g of glucose and 20 g of sodium hydroxide in 200 g of distilled water. The corrosion layer was retained on the surface of the other corroded electrode, and the morphology of the corrosion layers and corroded surfaces of the Pb and Pb–Te alloy electrodes were analyzed using a JSM-6380 scanning electron microscope (SEM).

3. Results and discussion

3.1. Microstructure of Pb–Te binary alloys

By means of a polarizing microscope, the microstructures of Pb and Pb–Te binary alloys with different Te content were observed and are presented in Fig. 1. Pb generates a large grain size with anomalous grain boundaries; a similar morphologic structure was observed with the Pb–0.01 wt.%Te alloy. The Pb–0.03 wt.%Te alloy has a fine grain and regular boundaries, which can protect the lead alloy from being recrystallized and hence improve the stability of the structure compared with that of pure Pb. With the increase of Te

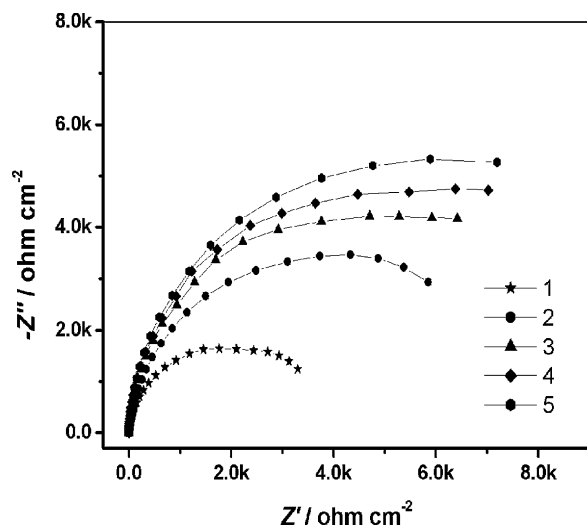


Fig. 3. Nyquist plots of the impedance data for Pb and Pb–Te electrodes in 1.28 g cm^{-3} H_2SO_4 solution at 1.3 V. 1, Pb; 2, Pb–0.01 wt.%Te; 3, Pb–0.03 wt.%Te; 4, Pb–0.3 wt.%Te; 5, Pb–1.0 wt.%Te.

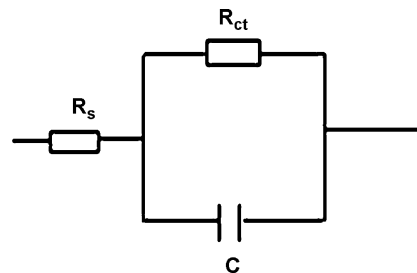


Fig. 4. The electrical equivalent circuit used to fit the impedance data of Pb and Pb–Te alloys from Fig. 3.

content (more than 0.03 wt.%), the Pb–Te binary alloys show similar structure with fine grain. This study indicates that Te plays an important role on the structure of lead alloys, and the appropriate content of Te in Pb–Te alloys may result in a fine grain stable structure.

3.2. PbO_2 formed on Pb–Te binary alloys

PbO_2 is the major product of anodic corrosion. The amount of PbO_2 can be used to evaluate the extent of corrosion of the positive grid alloy. Therefore, the electrochemical experiments focused upon the formation of PbO_2 on Pb–Te alloys in sulfuric acid solution. A potential of 1.3 V was chosen for the OCP and EIS tests, because 1.3 V is the growth potential for PbO_2 on the positive grid alloys when the battery is undergoing a float charge.

3.2.1. Open circuit potential (OCP)

The open circuit potential decay curves of the Pb and Pb–Te electrodes with different Te content are shown in Fig. 2. The working electrodes were charged at 1.3 V for 1 h to form PbO_2 films on the alloy surfaces, and the decay curves of potential vs. time were recorded in an open circuit condition. An induction period at 1.12 V appears before a rapid potential decay to a quasi-steady value (-0.4 V). The induction period is attributed to the transformation of PbO_2 into PbSO_4 during the self-discharging process [6]. The induction period time (T_{EF}) is associated with the amount of PbO_2 formed on the lead alloy during the charging process. As can be seen from Fig. 2, the T_{EF} values of Pb–Te electrodes are shorter than that of the pure Pb electrode, and decrease with increasing Te content. It is concluded that Te can inhibit the growth of PbO_2 on lead alloys during charging.

3.2.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a steady-state technique used to study the oxide films on surfaces [7], and is frequently employed to investigate the characteristics of the oxide films on the surfaces of lead alloys. Impedance measurements for Pb and Pb–Te alloys were performed at a potential of 1.3 V over the range 100 MHz to 0.01 Hz with AC amplitude of 5 mV. Fig. 3 shows Nyquist plots of the impedance of the five electrodes, which may be described by the equivalent circuit model illustrated in Fig. 4. The

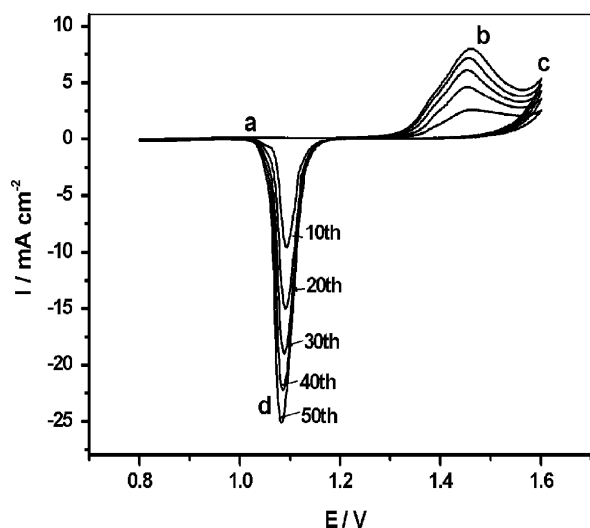
Table 2

Fitted values calculated from the impedance data of Pb and Pb–Te alloys using an equivalent circuit (Fig. 4)

Alloys	R_s ($\Omega \text{ cm}^{-2}$)	R_{ct} ($\text{k}\Omega \text{ cm}^{-2}$)	C
Pb	1.23	4.09	1.79
Pb–0.01 wt.%Te	1.80	8.16	1.49
Pb–0.03 wt.%Te	1.25	9.59	1.92
Pb–0.3 wt.%Te	1.98	10.95	1.26
Pb–1.0 wt.%Te	1.57	11.27	1.84

Table 3Cathodic reduction charges (Q_c) of the peak d in the cyclic voltammograms for Pb and Pb–Te electrodes

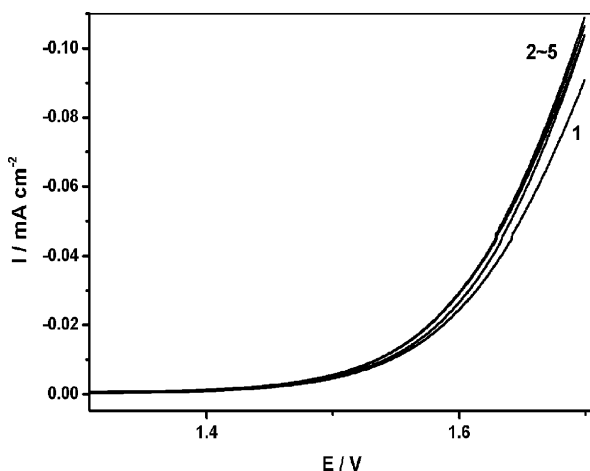
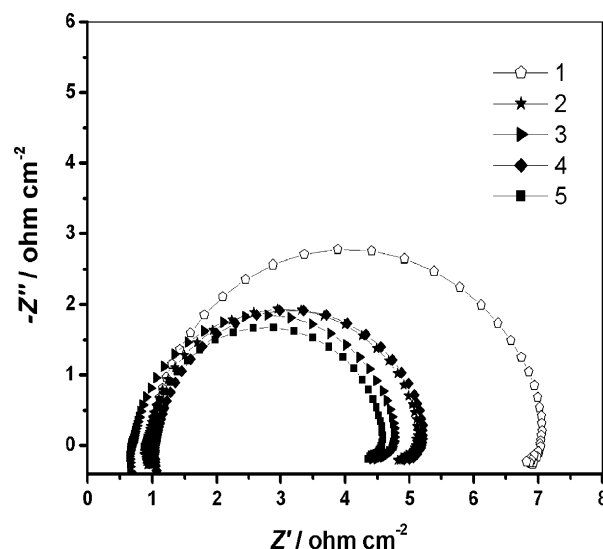
Cycles (N)	Q_c (mC cm ⁻²) Pb	Pb–0.01 wt.%Te	Pb–0.03 wt.%Te	Pb–0.3 wt.%Te	Pb–1.0 wt.%Te
10th	123	123	121	112	98
20th	204	194	196	168	146
30th	264	251	251	210	182
40th	318	299	297	246	211
50th	369	345	342	284	240
Growth rate (mC cm ⁻² N ⁻¹)	7.4	6.9	6.8	5.7	4.8

**Fig. 5.** Cyclic voltammograms for the Pb electrode in 1.28 g cm⁻³ H₂SO₄ solution for the 10th, 20th, 30th, 40th, 50th cycle (scan rate = 5 mV s⁻¹).

fitted values are listed in Table 2: R_s is the solution resistance; R_{ct} is the charge transfer resistance of PbO₂; and C is the double layer capacitance of the corrosion layer (PbO₂). From Table 2, the value of R_{ct} increases with Te content. It can be obtained that resistance of the corrosion reaction (formation of PbO₂) on the electrode surface increases with Te content. This result further suggests that Te can suppress the growth of PbO₂ on Pb–Te alloys.

3.2.3. Cyclic voltammetry (CV)

Fig. 5 shows the cyclic voltammograms of the Pb electrode in the 10th, 20th, 30th, 40th, and 50th cycles. During the positive sweep

**Fig. 6.** Anodic polarization curves of Pb and Pb–Te electrodes in 1.28 g cm⁻³ H₂SO₄ solution from 1.3 V to 1.7 V. 1, Pb; 2, Pb–0.01 wt.%Te; 3, Pb–0.03 wt.%Te; 4, Pb–0.3 wt.%Te; 5, Pb–1.0 wt.%Te (scan rate = 5 mV s⁻¹).**Fig. 7.** Nyquist plots of the oxygen evolution reaction on Pb and Pb–Te electrodes in 1.28 g cm⁻³ H₂SO₄ solution at 1.6 V. 1, Pb; 2, Pb–0.01 wt.%Te; 3, Pb–0.03 wt.%Te; 4, Pb–0.3 wt.%Te; 5, Pb–1.0 wt.%Te.

from 0.8 V to 1.6 V, three anodic peaks: a, b and c are observed. These correspond to: the oxidation of the Pb substrate to α -PbO₂; the transformation of PbSO₄ to β -PbO₂; and the evolution of oxygen, respectively. Meanwhile, a cathodic peak d corresponding to the reduction of PbO₂ appears in the negative sweep [8]. The four peaks a, b, c and d increase in magnitude with the increasing cycles. It was presumed that the increasing peak current was attributed to the porous corrosion layer formed on the electrode during the cyclic process, which results in a larger true surface area of the corrosion layer. Table 3 lists the cathodic reduction charges (Q_c) of peak d in the cyclic voltammograms for Pb and Pb–Te alloy electrodes. As can be seen from Table 3, Pb–Te electrodes have lower growth rates of Q_c than the Pb electrode, and the growth rate decreases with increasing Te content. It appears that Te can inhibit the growth of PbO₂ for a lead alloy in sulfuric acid solution. The conclusion is also consistent with the results from the ACV and EIS experiments (Figs. 2 and 3).

Table 4

The resistance and double layer capacitance for oxygen evolution on Pb and Pb–Te electrodes at 1.6 V

Alloys	R_{ct} (Ω cm ⁻²)	Capacitance
Pb	6.1	1.08
Pb–0.01 wt.%Te	4.2	1.03
Pb–0.03 wt.%Te	4.0	1.26
Pb–0.3 wt.%Te	4.1	1.29
Pb–1.0 wt.%Te	3.8	1.27

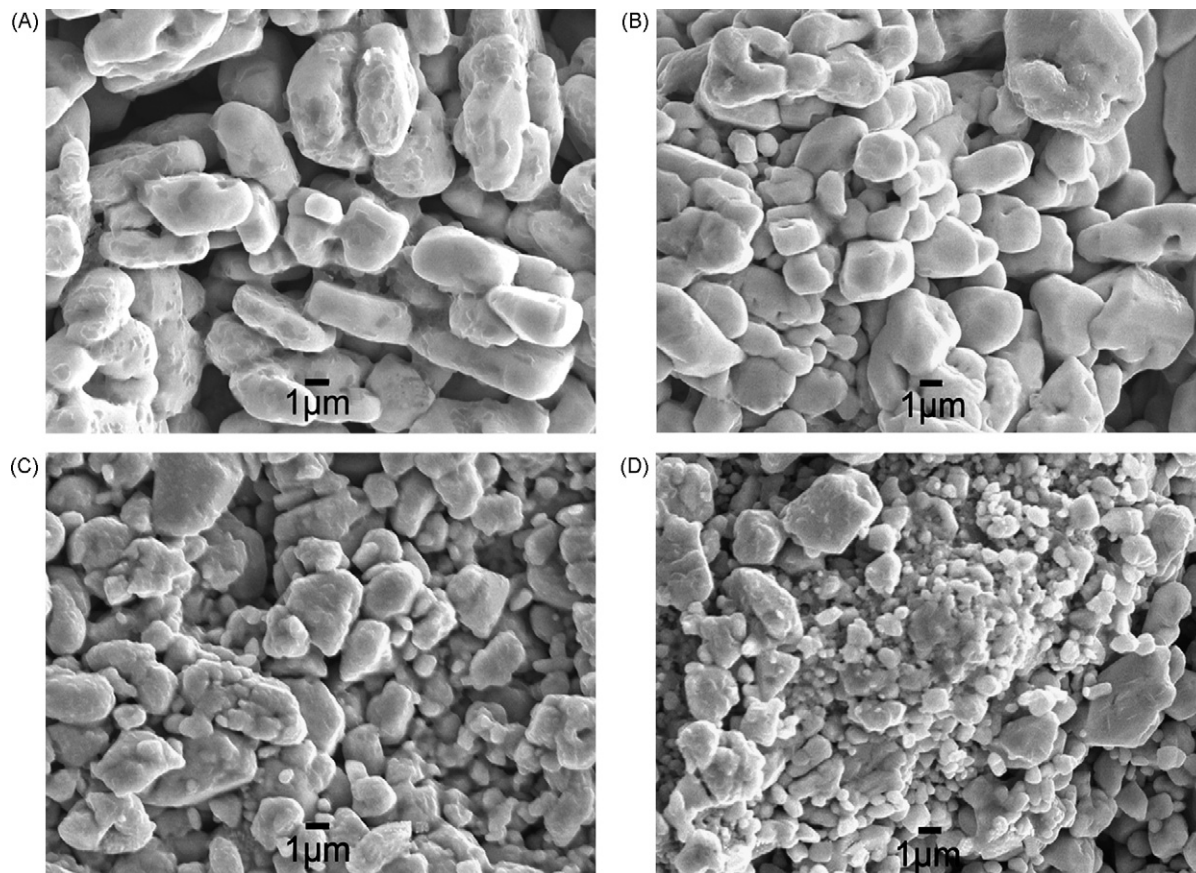


Fig. 8. Morphology of the corrosion layer of Pb and Pb–Te alloys after the corrosion test (5000 $\times$): (A) pure Pb; (B) Pb–0.03 wt.%Te; (C) Pb–0.1 wt.%Te; (D) Pb–0.3 wt.%Te.

3.3. Oxygen evolution for Pb–Te binary alloys

The rate of oxygen evolution was measured by LSV and EIS. Before the tests, the electrodes were polarized at 1.7 V for 40 min in 1.28 g cm^{−3} H₂SO₄ solution to form an anodic layer of β -PbO₂ [9]. The oxygen evolution occurs at the anodic layer-electrolyte interface, and the oxygen evolution rate is influenced by the quantity of PbO₂ on the electrode surface [10]. In the LSV test, the anodic polarization curves of the Pb and Pb–Te electrodes in 1.28 g cm^{−3} H₂SO₄ solution from 1.3 V to 1.7 V are shown in Fig. 6. It can be seen that the current of the Pb–Te electrodes are higher than that of the Pb electrode at the same potential. This result indicates that the Pb–Te alloy can accelerate the oxygen evolution reaction. In addition, curves 2–5 indicate that no significant change is found among the Pb–Te alloys as the Te content increases.

Fig. 7 shows the electrochemical impedance spectroscopy of the Pb and Pb–Te electrodes at 1.6 V. The plots of the five electrodes are similar and exhibit a semicircular part at high frequency, which means that the oxygen evolution reaction on the alloys is limited by the charge transfer step. The reaction resistance (R_{ct}) of oxygen evolution and the double layer capacitance obtained by fitting the experimental data with a Randles equivalent circuit [9] are listed in Table 4. It can be seen that Pb–Te electrodes exhibit a lower reaction resistance for oxygen evolution than the Pb electrode. Oxygen evolution is accelerated by the introduction of Te to lead. However, no obvious influence was observed on the oxygen evolution of Pb–Te alloys with Te content from 0.01 wt.% to 1.0 wt.%, this phenomenon is consistent with the LSV results (Fig. 6).

3.4. Corrosion test for Pb–Te binary alloys

The corrosion layers were observed after corrosion test of the Pb and Pb–Te alloys, and are illustrated in Fig. 8. The SEM micrographs reveal the differences in the morphology of the corrosion layers between the Pb and Pb–Te alloys. A loose and porous corrosion layer is formed on pure Pb, but a compact corrosion layer with fine corroded products can be observed on the Pb–Te alloys. The corrosion layer becomes more compact and the corroded products become finer as the Te content increases. The compact corrosion layer of Pb–Te alloys can protect the substrate lead of the alloys from corrosion by the electrolyte.

The extent of corrosion on lead alloys can be determined by the nature of the surface morphology [11]. As shown in Fig. 9, after removing the corrosion products, the morphology of the corroded surfaces of Pb and Pb–Te alloy electrodes show different corrosion behavior. It has been observed that uniform corrosion was throughout the surfaces of the Pb–Te alloys, because of their fine grain structure with much grain boundaries. The uniform corrosion may result in rough surface morphology on the Pb–Te alloys comparing with that of pure Pb. In particular, this is illustrated by the Pb–0.3 wt.%Te alloy. On the other hand, the surface of the pure Pb plate, with large grain, is smooth, and corrosion occurs preferentially along the grain boundaries. The cracks on the grain boundaries of pure Pb are deeper than those of Pb–Te alloys as can be seen in Fig. 10. This indicates that the Pb electrode suffers more serious intergranular corrosion than Pb–Te alloys. In addition, the microstructure of the cracks (Fig. 10) indicates that dendritic crystals occur at the grain boundaries of the corroded Pb–Te alloys, and the dendritic crystals may

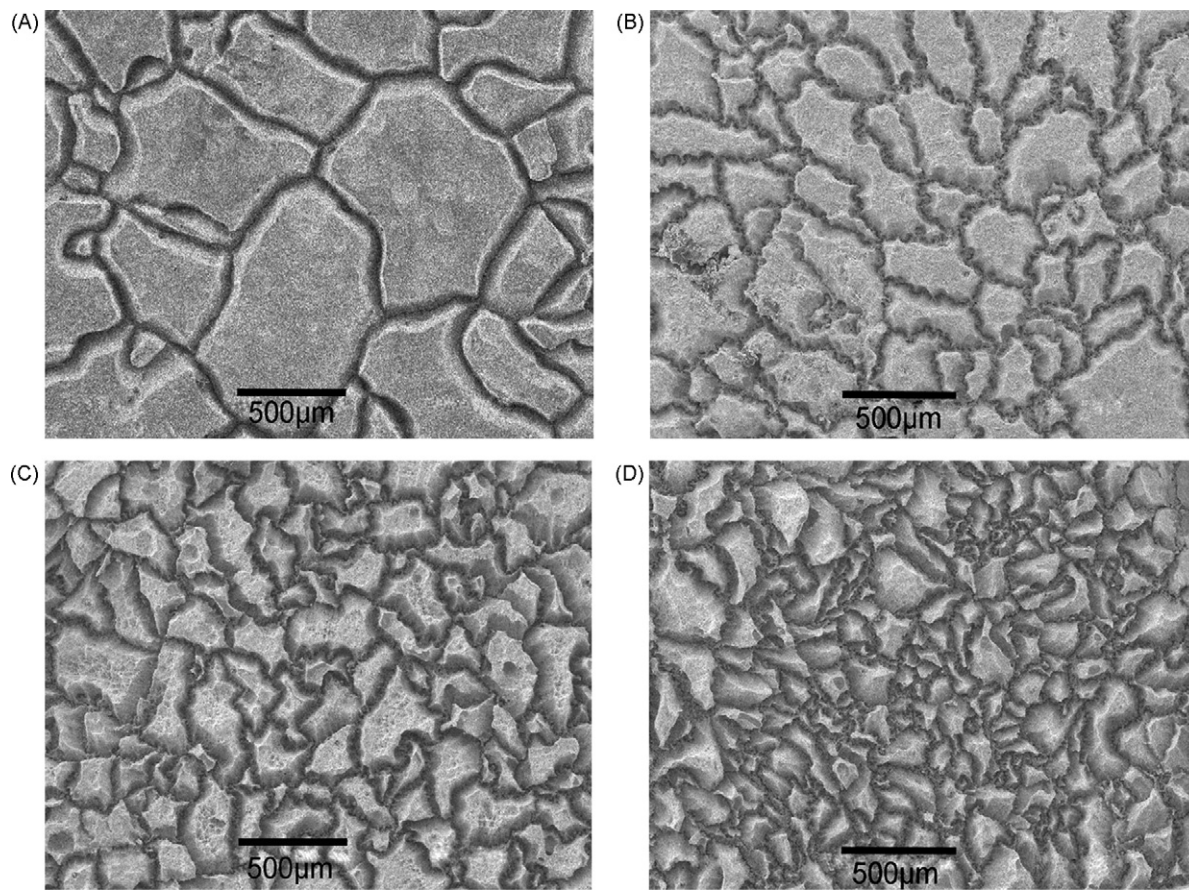


Fig. 9. Morphology of the corroded alloys following removal of the corrosion layer after the corrosion test (50 $\times$): (A) pure Pb; (B) Pb–0.03 wt.%Te; (C) Pb–0.1 wt.%Te; (D) Pb–0.3 wt.%Te.

consolidate the connection of each grain. Consequently, the introduction of Te to lead alloys can reduce the penetrable corrosion of the positive grid alloys, and result in a longer life for the battery.

3.5. Characteristics of the passive film formed on the Pb–Te–Sn alloy

The high impedance passive film composed of Pb(II) oxide between the positive grid and the active material is thought to be one cause of the premature capacity loss (PCL) of lead acid batteries [12,13]. In order to study the characteristics of the passive film on the surface of Pb–Te–Sn alloy, a potential of 0.9 V is chosen for the ACV, LSV and EIS tests, as this is the growth potential for PbO on the positive grid alloy following deep discharge.

3.5.1. Alternating current voltammetry (ACV)

Fig. 11 provides the plots of Z' (real part of the impedance) vs. potential (E) of the passive films formed on Pb–Te (Te: 0.03 wt.%), Pb–Te–Sn (Te: 0.03 wt.%, Sn: 0.9 wt.%) and Pb–Ca–Sn (Ca: 0.08 wt.%, Sn: 0.9 wt.%) electrodes at 0.9 V in 1.28 g cm $^{-3}$ H $_2$ SO $_4$ solution for 1 h. During the negative sweep from 0.7 V to -1.2 V, the Z' remains at a high level until about -0.8 V, then drops dramatically to a low level, corresponding to the change from highly resistive Pb(II) oxide film to electrically conductive Pb metal. It is demonstrated that the resistance of the passive film on a Pb–Te–Sn electrode is less than that on a Pb–Te electrode by comparing curves 1 and 2 in Fig. 11. This indicates the resistance of the passive film decreases with the introduction of Sn to the Pb–Te binary alloy. This is because that

the Sn in the lead alloy is present in the PbO layer in two forms: SnO $_2$ is precipitated at the grain boundaries; and Sn(II) is substituted for Pb(II) in the tetragonal PbO lattice [14], which results in a lower resistance of the Pb(II) oxide film. Comparing curves 2 and 3 in Fig. 11, the resistance of the passive film on the Pb–Te–Sn electrode is lower than that on the Pb–Ca–Sn electrode. It is thought that in sulfuric acid solution Ca is transformed into CaSO $_4$, which has a similar lattice parameter to that of PbSO $_4$. Therefore CaSO $_4$ acts as the nucleus for crystallization and can accelerate the growth rate of PbSO $_4$, which has poor conductivity [15]. In this case, substitution of the Te for Ca in the Pb–Ca–Sn alloy may improve the conductivity of the interface between the grid and the active material.

3.5.2. Linear sweeping voltammetry (LSV)

Fig. 12 shows the voltammograms of passive films formed on Pb–Te, Pb–Te–Sn and Pb–Ca–Sn electrodes at 0.9 V for 1 h in 1.28 g cm $^{-3}$ H $_2$ SO $_4$ solution. Two peaks appear in the negative sweep for each electrode: peaks A and B, corresponding to the reduction of Pb(II) oxides to Pb, and PbSO $_4$ to Pb, respectively. The potentials and currents of each peak are listed in Table 5, and the

Table 5

Parameters of the peak potential and peak current for Pb–Te, Pb–Te–Sn and Pb–Ca–Sn electrodes in the LSV test (Fig. 12)

Electrodes	E_A (V)	I_A (mA cm $^{-2}$)	E_B (V)	I_B (mA cm $^{-2}$)
Pb–Te	-0.927	8.21	-0.985	3.82
Pb–Te–Sn	-0.930	6.81	-0.981	2.63
Pb–Ca–Sn	-0.932	10.8	-0.976	2.59

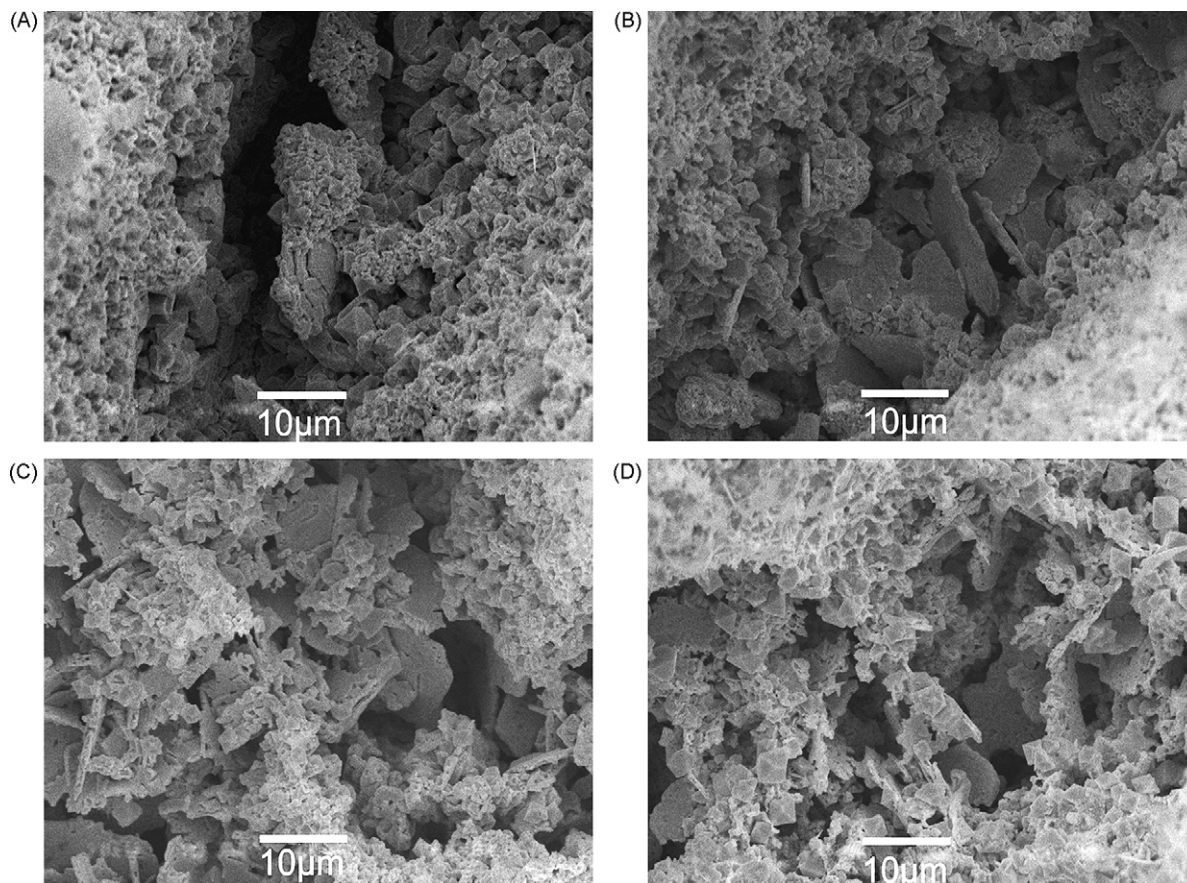


Fig. 10. Morphology of the cracks on grain boundaries following removal of the corrosion layer (2000 $\times$): (A) pure Pb; (B) Pb-0.03 wt.%Te; (C) Pb-0.1 wt.%Te; (D) Pb-0.3 wt.%Te.

current of peak A for a Pb-Te-Sn electrode is lower than that of both the Pb-Te and Pb-Ca-Sn electrodes. This suggests that the introduction of Sn into a Pb-Te binary alloy can inhibit the growth of Pb(II) oxides, and the substitution of Te for Ca in the traditional Pb-Ca-Sn alloy may also result in lower growth of Pb(II) oxides.

3.5.3. Electrochemical impedance spectroscopy (EIS)

The impedance spectra of passive films formed on Pb-Te, Pb-Te-Sn and Pb-Ca-Sn electrodes at 0.9 V for 1 h in 1.28 g cm⁻³ H₂SO₄ solution are shown in Fig. 13. The spectra of the three electrodes has a similar shape. At the high frequency, the semicircle corresponds to the charge transfer resistance. At the low frequency,

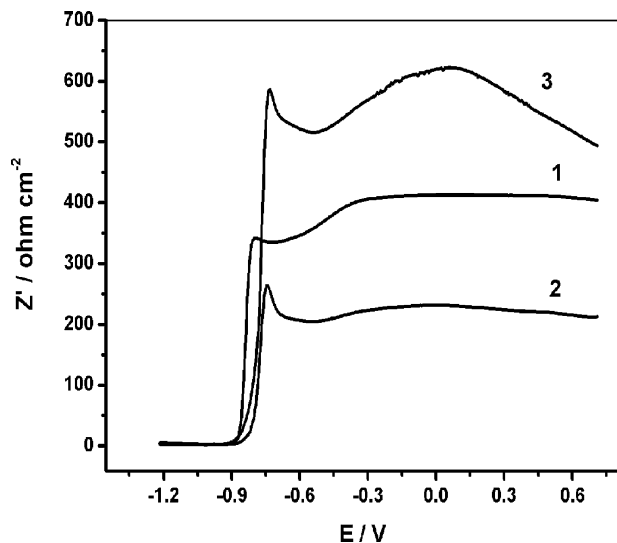


Fig. 11. Z' vs. E plots for the passive films formed on Pb-Te, Pb-Te-Sn and Pb-Ca-Sn electrodes at 0.9 V in 1.28 g cm⁻³ H₂SO₄ solution for 1 h. 1, Pb-0.03 wt.%Te; 2, Pb-0.03 wt.%Te-0.9 wt.%Sn; 3, Pb-0.08 wt.%Ca-0.9 wt.%Sn.

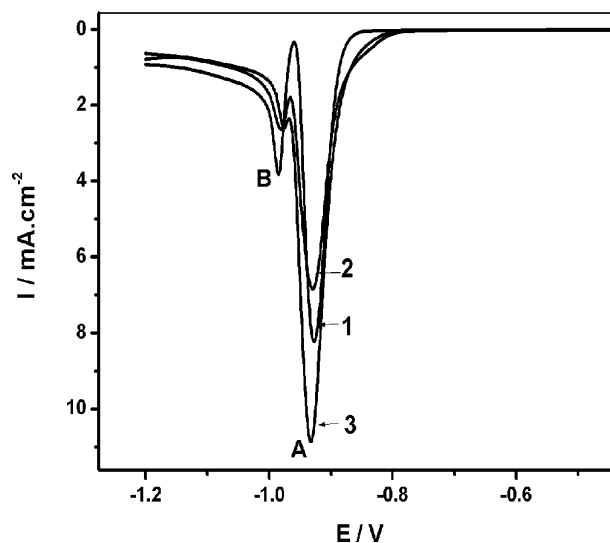


Fig. 12. Voltammograms of the passive films formed on Pb-Te, Pb-Te-Sn and Pb-Ca-Sn electrodes at 0.9 V in 1.28 g cm⁻³ H₂SO₄ solution for 1 h. 1, Pb-0.03 wt.%Te; 2, Pb-0.03 wt.%Te-0.9 wt.%Sn; 3, Pb-0.08 wt.%Ca-0.9 wt.%Sn.

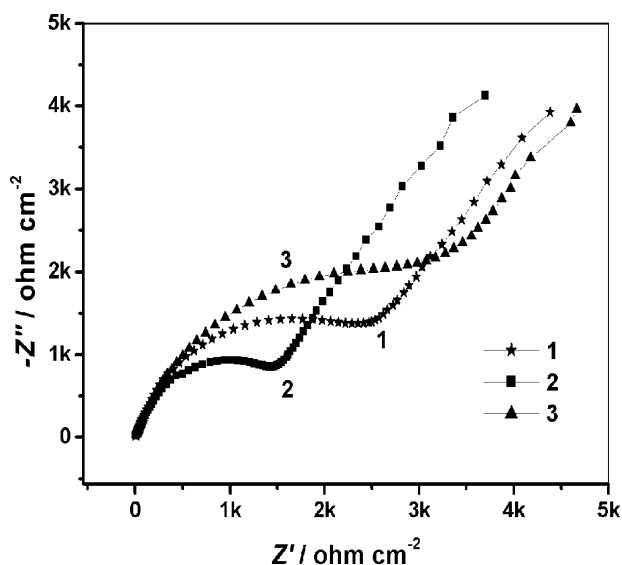


Fig. 13. Nyquist plots of the impedance data for Pb–Te, Pb–Te–Sn and Pb–Ca–Sn electrodes in 1.28 g cm^{-3} H_2SO_4 at 0.9 V for 1 h. 1, Pb–0.03 wt.%Te; 2, Pb–0.03 wt.%Te–0.9 wt.%Sn; 3, Pb–0.08 wt.%Ca–0.9 wt.%Sn.

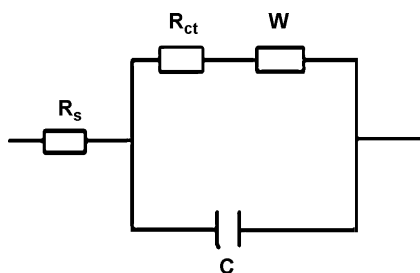


Fig. 14. The electrical equivalent circuit used to fit the impedance data of Pb–Te, Pb–Te–Sn and Pb–Ca–Sn electrodes from Fig. 13.

Table 6

Fitted values calculated from the impedance data of Pb–Te, Pb–Te–Sn and Pb–Ca–Sn electrodes at 0.9 V using an equivalent circuit (Fig. 14)

Electrodes	R_{ct} ($\Omega \text{ cm}^{-2}$)	W ($\times 10^{-4} \Omega \text{ cm}^{-2}$)
Pb–Te	2.25	2.14
Pb–Te–Sn	1.32	2.50
Pb–Ca–Sn	2.82	0.93

the straight line represents diffusion-controlled process, which is the characteristic of Warburg impedance. Fitted values, calculated by using the equivalent circuit in Fig. 14 are listed in Table 6. R_{ct}

is the electrochemical impedance of the oxide on the electrodes, and W is the Warburg impedance. The R_{ct} value of the Pb–Te–Sn electrode is lower than those of the Pb–Te and Pb–Ca–Sn electrodes, indicating that less Pb(II) oxide is formed on the Pb–Te–Sn electrodes. This result is consistent with those from ACV and LSV (Figs. 11 and 12).

4. Conclusion

The fine grain size and regular grain boundaries obtained in Pb–Te binary alloys (with $\text{Te} \geq 0.03 \text{ wt.}\%$) may protect the lead alloy from recrystallization.

The results of electrochemical experiments show that the introduction of Te can inhibit the growth of PbO_2 for Pb–Te alloys in sulfuric acid solution, and increase their corrosion resistance when used as positive grid alloy.

Oxygen evolution is accelerated by the introduction of Te to lead, but no significant difference was found among the Pb–Te alloys with various Te content during the range investigated.

The corrosion product of Pb–Te binary alloys is fine and compact, and the introduction of Te may reduce the penetrable corrosion for positive grid alloys.

The introduction of Sn to a Pb–Te alloy can inhibit the growth of passive films on the alloy surface. In addition, the Pb(II) oxide passive films of the Pb–Te–Sn alloy show lower resistance characteristics than the traditional Pb–Ca–Sn alloy.

References

- [1] J. Furukawa, Y. Nehyo, S. Shiga, *J. Power Sources* 133 (2004) 25–31.
- [2] H.T. Liu, J. Yang, H.H. Liang, J.H. Zhuang, W.F. Zhou, *J. Power Sources* 93 (2001) 230–233.
- [3] Y.B. Zhou, C.X. Yang, W.F. Zhou, H.T. Liu, *J. Alloys Compd.* 365 (2004) 108–111.
- [4] R.D. Prengaman, *J. Power Sources* 95 (2001) 224–233.
- [5] E. Bashtavelova, A. Winsel, *J. Power Sources* 67 (1997) 93–103.
- [6] A.G. Gad Allah, H.A. Abd El-Rahman, M. Abd El-Galil, *J. Power Sources* 62 (1996) 51–57.
- [7] D. Slavkov, B.S. Haran, B.N. Popov, F. Fleming, *J. Power Sources* 112 (2002) 199–208.
- [8] H.T. Liu, X.H. Zhang, Y.B. Zhou, C.X. Yang, W.F. Zhou, *J. Mater. Lett.* 57 (2003) 4597–4600.
- [9] W.S. Li, H.Y. Chen, X.M. Long, F.H. Wu, Y.M. Wu, J.H. Yan, C.R. Zhang, *J. Power Sources* 158 (2006) 902–907.
- [10] S. Zhong, J. Wang, H.K. Liu, S.X. Dou, *J. Appl. Electrochem.* 29 (1999) 1–6.
- [11] C.S. Lakshmi, J.E. Manders, D.M. Rice, *J. Power Sources* 73 (1998) 23–29.
- [12] A.F. Hollemkamp, K.K. Constanti, M.J. Koop, L. Aputeanu, *J. Power Sources* 48 (1992) 125.
- [13] D. Pavlov, *J. Power Sources* 48 (1994) 179.
- [14] A. El Ghachcham Amrani, Ph. Steyer, J. Steinmetz, P. Delcroix, G. Le Caër, *J. Power Sources* 64 (1997) 35–37.
- [15] D.G. Li, G.S. Zhou, G.F. Lin, M.S. Zheng, *J. Rare Earths* 23 (2005) 353–357.